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# Performance of Adsorbents at Various Relative Humidities

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Test tube-sized samples of an activated coconut charcoal, Whetlerite, and a pyrolyzed synthetic resin-based adsorbent were challenged with benzene and with methyl ethyl ketone (MEK) vapors in a flowing system at a range of relative humidity from 0 to 95%. The time to initial break, time to equilibrium, and sorptive capacity were observed. In general, although MEK is soluble in water as opposed to benzene being insoluble, adsorbent performance was similar for both vapors. In both cases, adsorbent performance showed marked deterioration above 50% relative humidity. K P 1000000					
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# PERFORMANCE OF ADSORBENTS AT VARIOUS RELATIVE HUMIDITIES

## INTRODUCTION

This study was initiated to show the effects of relative humidity on adsorbent performance. Since marine environments generally have higher relative humidities than those encountered on land, knowledge of the effects of relative humidity on adsorbent performance is of prime importance to the Navy. The current study also addressed some of the effects of gas flow rates on adsorption. Flow rates were varied from 2.4 l/min (40 linear ft/min), which corresponds roughly to heavy breathing in a gas mask, to 6 l/min (100 linear ft/min), which is common for many powered air filtration systems. Relative humidity was varied from 0 to 95%.

## EXPERIMENTAL

Figure 1 is a diagram of the humidified/dry air test system. Compressed air, cleaned and dried by passage through charcoal and Drierite<sup>®</sup> columns, passed through a flow meter and mixing chamber and then either through the sample tube or a by-pass to a photoionization detector. For the humidified runs, the clean dry air was diverted through a supplemental loop, where water was injected into the air stream with a motorized syringe pump. Relative humidity was measured with an electric hygrometer. The hygrometer was calibrated in the system by comparison with wet bulb/dry bulb thermometer readings taken at the effluent end of the system. Agreement between these instruments was within approximately  $\pm 1\%$  RH.

The contaminants were also introduced by syringe pump injection at a concentration of 350-400 ppm by volume. Contaminant concentration was measured with a photoionization detector. It was found that water vapor had a masking effect on the output of the photoionization detector. Hence, calibration runs had to be made on the detector for each contaminant over the full humidity range. This masking effect was reproducible, so that one calibration sufficed for each contaminant. The adsorbent beds were equilibrated to the chosen relative humidity for each run prior to introduction of the contaminant vapor. Thus, the experiments were performed under, perhaps, the worst situation, but one that probably was close to actual operating conditions.

The choice of contaminants, benzene and methyl ethyl ketone (MEK), was somewhat arbitrary--dictated partially by the high sensitivity of the photoionization detector for these compounds, and partially by the fact that these could provide performance comparisons between (a) a water insoluble and a water soluble contaminant and (b) an aromatic and an aliphatic compound.

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The choice of contaminant is less important, however, in view of a study of charcoal breakthrough data from the Lawrence Livermore Laboratory (LLL)<sup>1</sup>, which suggests that contaminant choice is not critical. In that study, canisters containing untreated activated charcoal were challenged with a variety of organic solvent vapors (120 compounds, including aromatics, organic halides, alcohols, acetates, ketones, and amines with boiling points from -25 to +175°C and molecular weights from 30 to 200 g/mole). Concentration was 500 ppm, flow rate was 3.5 l/min, and relative humidity was 50%. Analysis of the LLL breakthrough data indicated that all the examples satisfied the following correlation equation:

$$10\% \text{ BT} = C T_b A$$

$$10\% \text{ BT} = 53 T_b A,$$

where

10% BT = 10% breakthrough time (min);  
i.e., the time at which effluent  
concentration is 10% of inlet  
concentration.

C = Constant = 53 (Depends upon a system's  
geometry, flow rate,  
concentration, etc.)

$T_b$  = Boiling point (°K) of contaminant

A = Moles adsorbed at equilibrium per gram  
adsorbent (moles/g)

Selected results from the LLL study are shown in Table 1. Experimental breakthrough times are compared to those calculated by the foregoing correlation equation. Results showing greatest deviation may reflect some differences due to solubility, reaction, or decomposition. Most differences, however, appear to be minor; otherwise, the correlation equation would not have fit so many examples.

The correlation equation, with the appropriate C-value for our system, holds true for our experimental results within  $\pm 5\%$ . However, our data at present are too sparse for full evaluation. More data will be required for full substantiation. If the correlation equation ultimately proves applicable to simulants and other chemical agents, the choice of a contaminant suitable for many studies may not be critical.

## RESULTS

Adsorption data versus flow rate at 0% relative humidity are shown in Figures 2 and 3 for Pittsburgh PCB (coconut) charcoal, ASC Whetlerite (Pittsburgh BPL coal-base, catalyst-impregnated charcoal), and a pyrolyzed synthetic resin-based adsorbent (Rohm & Haas Ambersorb<sup>®</sup> XE-348), with benzene as contaminant. Figure 2 shows breakthrough time (defined as the time of appearance in the effluent of 10 ppm, or approximately 3% of inlet concentration of 350-400 ppm) versus flow rate. The breakthrough time was only moderately affected by flow rate change from 3.5 to 6 l/min, but

at lower flow rates the breakthrough time was significantly longer. Figure 3 indicates that the weight percent adsorbed at equilibrium is relatively constant over the entire flow range. The results for MEK as contaminant were similar to those for benzene, as indicated in Table 2, which compares adsorbent data for benzene and MEK at various rates on Whetlerite.

Table 1. Correlation of breakthrough time with boiling point and molecular weight for various liquids.  
(Selected examples from 120 total)<sup>1</sup>

Solvent	10% BT (min)		Obs-calc (min)	Obs-calc (%dev)
	calc.	obs.		
Benzene	78	89	+11	+12
Toluene	104	114	+10	+ 9
Propyl alcohol	126	111	-15	-14
Pentanol	137	130	- 7	- 5
Ethyl Chloride	11	11	0	0
1,2-dichlorobutane	137	129	- 8	- 6
Chloroform	61	52	- 9	-17
CCl <sub>4</sub>	82	90	+ 8	+ 9
Methyl acetate	50	46	- 4	- 8
Propyl acetate	99	99	0	0
Acetone	41	46	+ 5	+11
2-Heptanone	110	114	+ 4	+ 4
Hexane	70	65	- 5	- 7
Heptane	85	90	+ 5	+ 5
Methylamine	18	18	0	0
Propylamine	97	111	+14	+13
1-Nitro propane	154	164	+10	+ 6
2-Ethoxyethanol	143	123	-20	-16
For 120 Compounds		Mean	+ 8	+ 8
		Mean	+ 9	+ 10



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Table 2. Comparison of benzene and MEK adsorption data in Whetlerite versus flow rate at 0% RH.

Flow Rate (l/min)	Breakthrough Time (min)		Wt% ads at Breakthru		Wt% ads at Equilibrium		Additional time to Equil (min)	
	Benzene	MEK	Benzene	MEK	Benzene	MEK	Benzene	MEK
6.0	41	41	8.7	8.3	15.5	12.9	42	44
4.8	38	37	-	7.4	15.1	-	52	-
3.6	75	64	-	8.1	14.8	-	62	-
2.4	168	113	10.6	9.6	13.0	11.7	106	90

Figures 4, 5, and 6 illustrate the adsorption data versus relative humidity for the above three adsorbents and the two contaminants at the 6 l/min flow rate. The group of curves ending in the lower right portion of the plot shows the breakthrough times, and the upper set of curves reflects the weight percent adsorbed at equilibrium. Figure 7 provides similar adsorption data for benzene at 2.4 l/min. Although adsorption tests were not run over the full humidity range for MEK at 2.4 l/min, the results for several selected runs indicated that behaviour for MEK was similar to that for benzene.

Figure 8 shows the breakthrough times plotted against relative humidity for our 6 l/min benzene and MEK results for Whetlerite, and also data from LLL for benzene, hexane, carbon tetrachloride, and acetone<sup>2</sup>. Although these LLL results were obtained from a different charcoal, at a lower flow rate (3.5 l/min), and a different bed configuration, the trend of significant decreases in breakthrough time with increasing relative humidity is clearly similar to that shown by our data.

Attempts were made by various methods to determine the respective amounts of contaminant and water present in a particular sample run at a particular relative humidity. Mass spectrometer and gas chromatographic studies gave only qualitative information as to the respective amounts of benzene and water contained in a sample. Thermal separation also proved to be inconclusive. Charcoal samples that contained either water or benzene alone could be regenerated easily by heating, but samples containing both adsorbates could not. Solvent extraction techniques as a means of separation also were inconclusive. Consequently, the respective amounts of contaminant and water were deduced by a mathematical analysis using assumptions based upon the 0% relative humidity runs. Two methods of calculation were followed.

The first analytical method involved determining the average weight of contaminant adsorbed per minute to equilibrium at 0% relative humidity and assuming that this rate of adsorption was

the same during the humidified runs. This determination provided a weight percent of the contaminant that would be adsorbed at a particular relative humidity. Subtracting this quantity from the total weight percent adsorbed yielded a weight percent difference for adsorbed water.

The second method involved determination of percent of contaminant adsorbed to equilibrium at 0% relative humidity, and then assuming that this fraction was applicable for the humidified runs. Then, by determining how much of the total amount was adsorbed to equilibrium, a value for the weight percent contaminant could be determined, and the difference from the observed total weight percent adsorbed could provide a value for the weight percent water at a particular relative humidity and ultimately the percent water in the total weight adsorbed.

Application of these analyses to each contaminant-adsorbent combination thus provided a mean value for the amount of water adsorbed at a particular relative humidity. Although the results are dependent upon the above assumptions, they do provide an approximation for the amount of water adsorbed vs. the amount of contaminant adsorbed at a particular relative humidity. Credibility of this approximation is further enhanced by Figure 9, which shows a plot of values for percent water in total adsorbate vs. relative humidity. This is accompanied by a plot of wet bulb/dry bulb temperature differences at 25°C vs. relative humidity<sup>3</sup>. The slopes are somewhat similar, as might be expected.

#### DISCUSSION AND CONCLUSIONS

Under variable flow conditions (2.4 to 6.0 l/min) the weight percent adsorbed at equilibrium for coconut base charcoal, Whetlerite, and a pyrolyzed synthetic resin-based adsorbent varied by only small amounts when challenged with 350-400 ppm benzene or MEK. Breakthrough times from 3.5 to 6.0 l/min also demonstrated only small variations, but at lower flow rates breakthrough times were much longer.

More data must be collected to establish the validity of the breakthrough correlation equation discussed early in this report. Recent studies by Kamlet, Doherty, Abraham, and Taft<sup>4</sup> on solvation energy parameters indicate that adsorbability on carbon increases with increasing molar volume of adsorbate. Their work also suggests a possible relationship between "hydrogen bonding basicity" and adsorbability. The effect of such parameters may well be implicit in the above correlation equation, and may be a useful topic for further study.

Under humid conditions, increasing humidity produced moderate increases in total weight percent adsorbed at equilibrium for all three adsorbents and both contaminants, with little difference, if any, between water-soluble MEK and water-insoluble benzene. Significant decreases, however, were evident in contaminant breakthrough times as relative humidity increased above 60-70%. Again, water solubility or insolubility of the contaminant seemed to be of little consequence.

Consequently, it appears that adsorbent bed life will be drastically reduced in high humidity environments, because the adsorbent will already contain or will acquire a high percentage of water. The decreased bed life due to humidity will probably have greater impact on systems that are continuously operating under high flow rates, such as collective filtration units, and less, though significant, impact on low-flow intermittent systems such as personal protective masks. In either case, adsorbent protection can be expected to be considerably less in high humidity conditions unless the adsorbed contaminants are destroyed or neutralized by processes other than or in addition to physical adsorption.

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4. Kamlet, M.J., Doherty, R.M., Abraham, M.H., and Taft, R.W., (Informal communication).

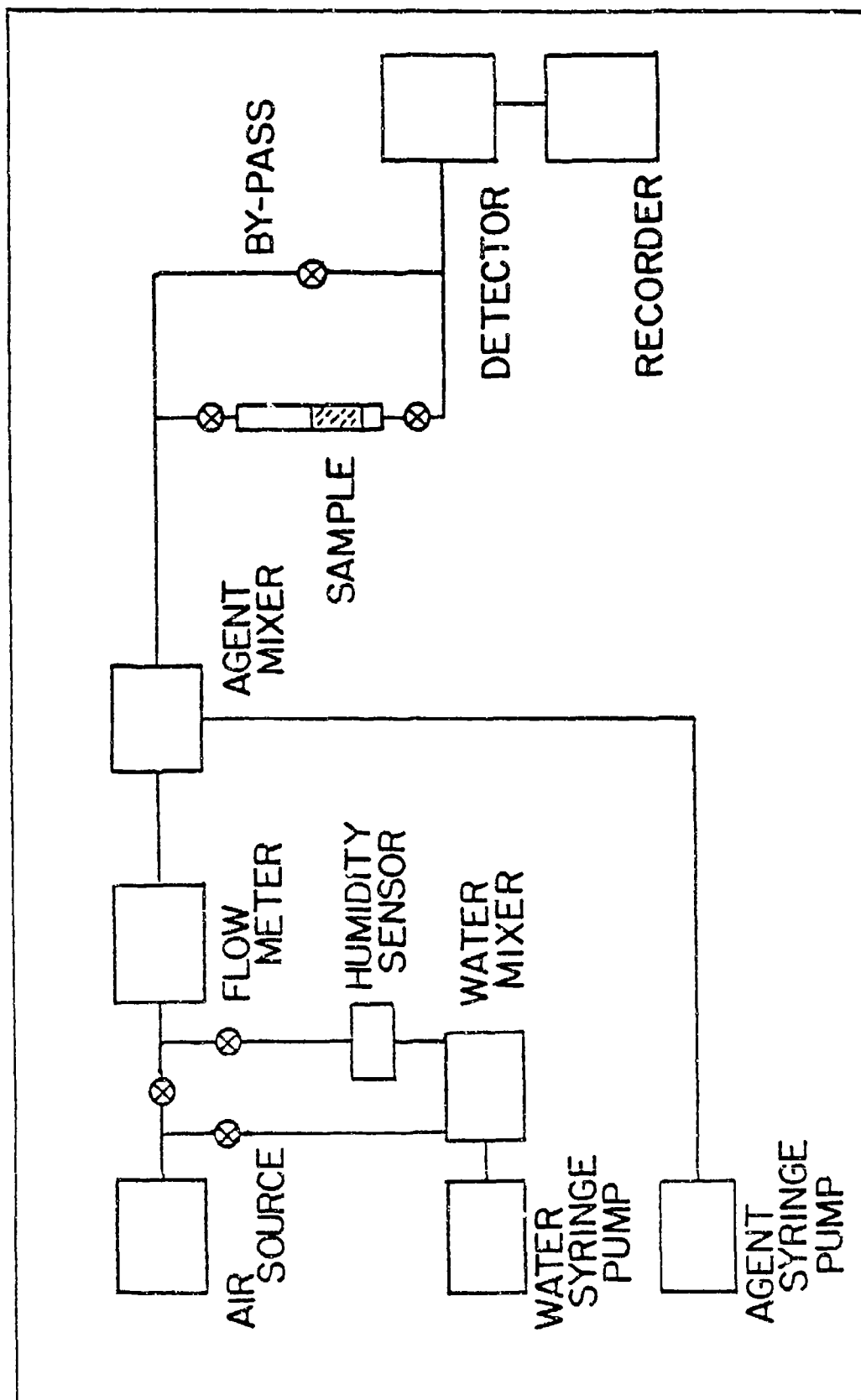


Fig. 1 — Schematic diagram of apparatus

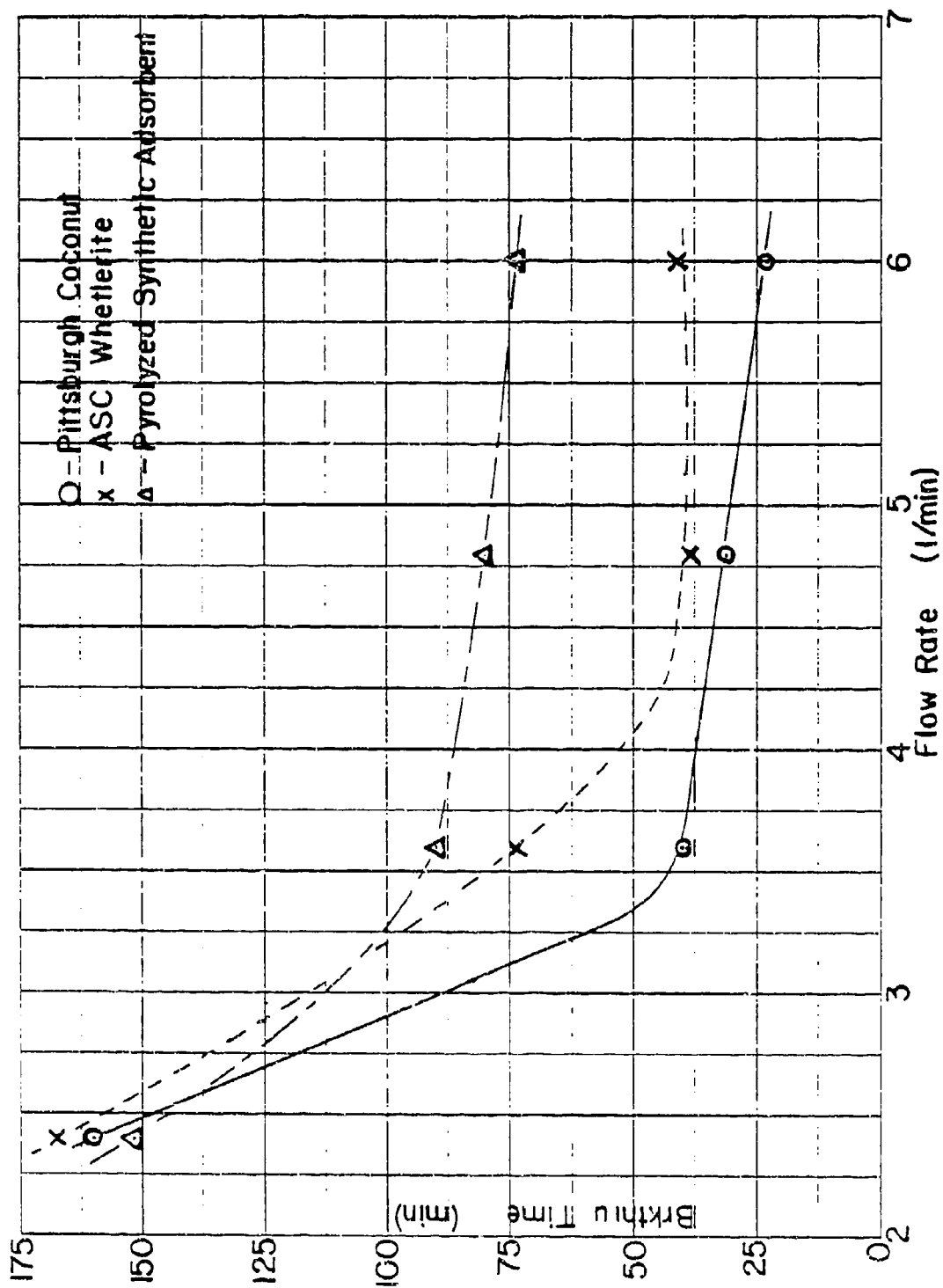


Fig. 2 — Breakthrough time as a function of flow rate at 0% relative humidity

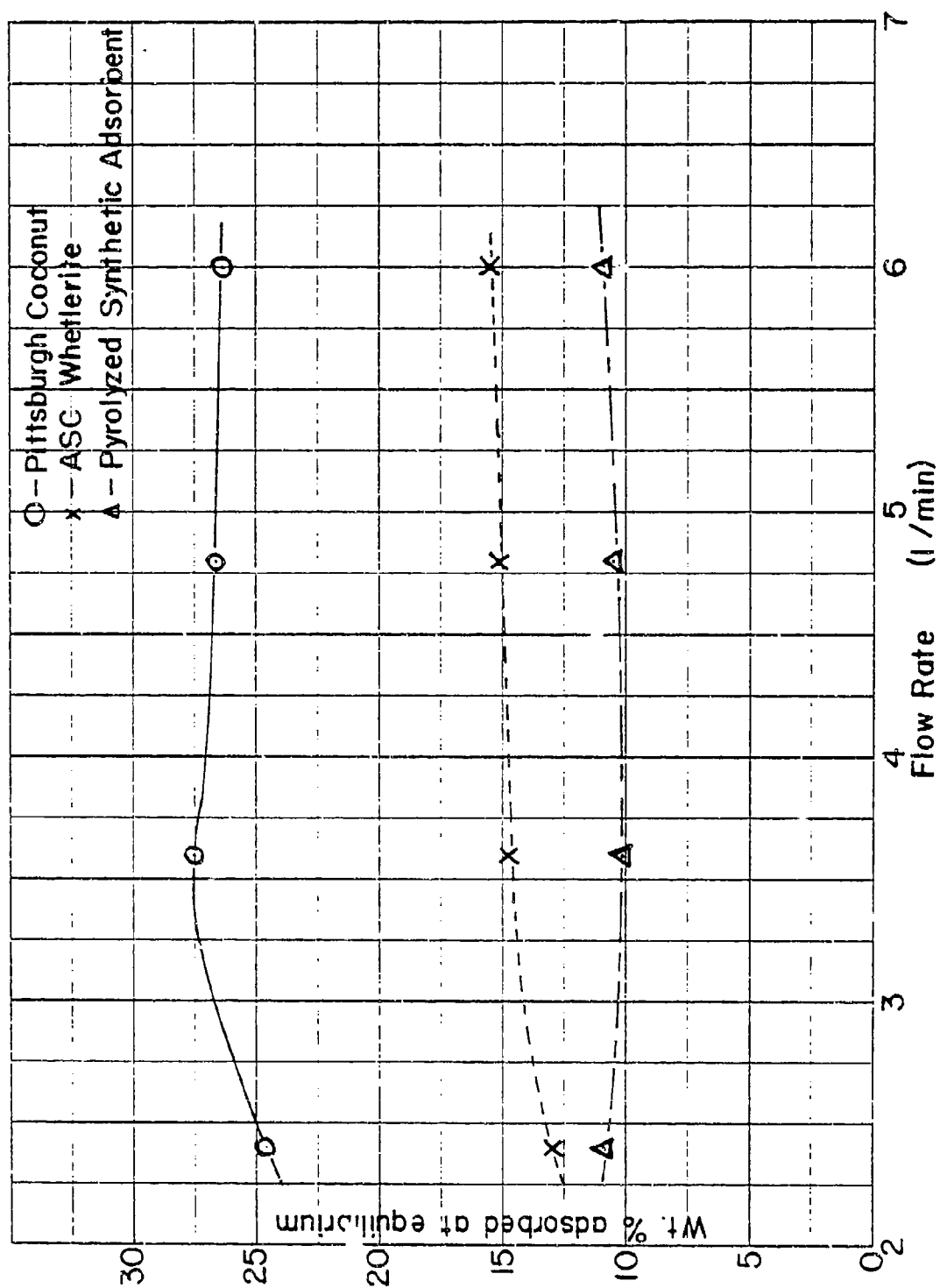


Fig. 3 — Weight percent adsorbed as a function of flow rate at 0% relative humidity

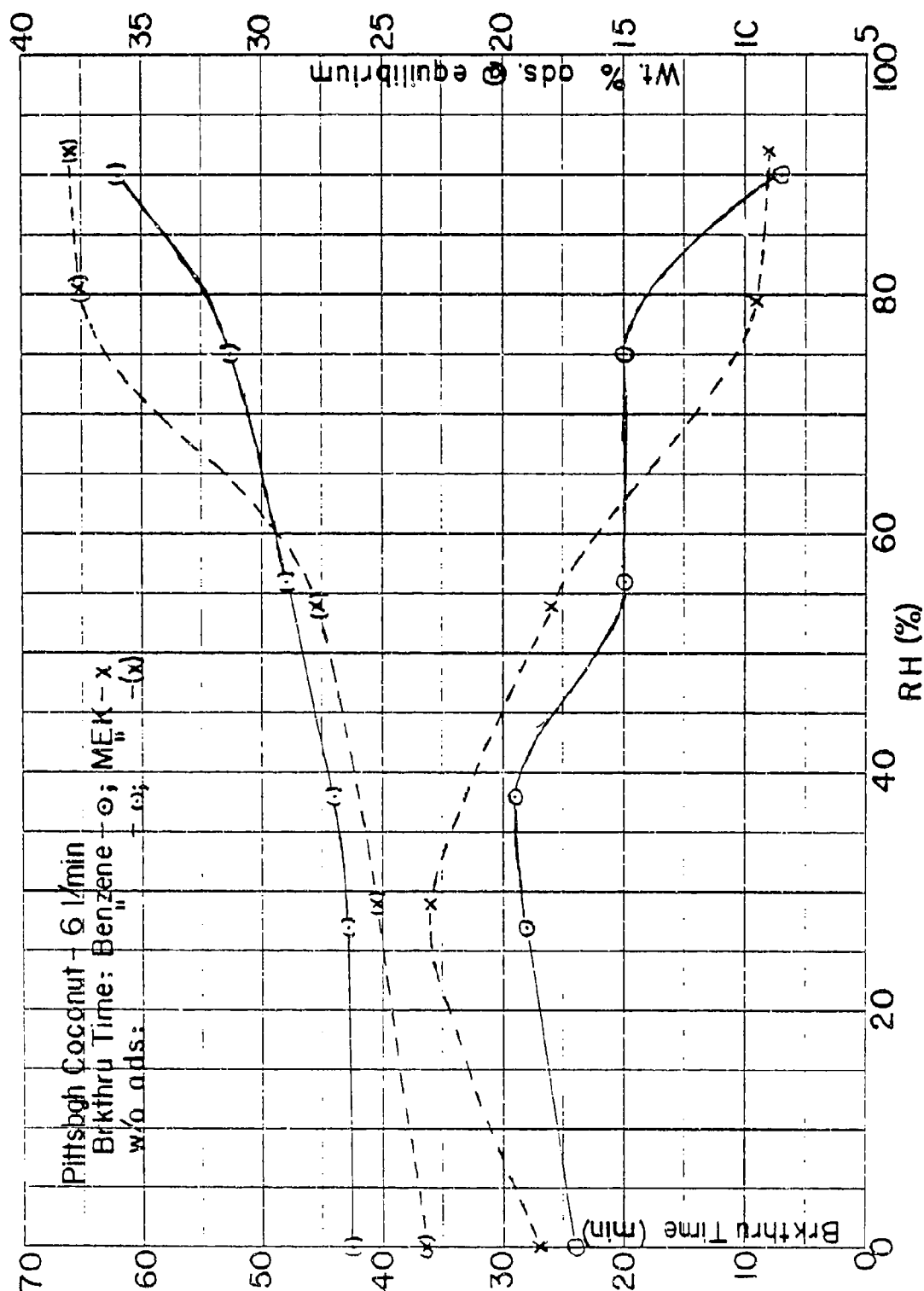


Fig. 4 — Breakthrough time and weight percent adsorbed as functions of relative humidity (Pittsburgh coconut charcoal, 6 l/min)

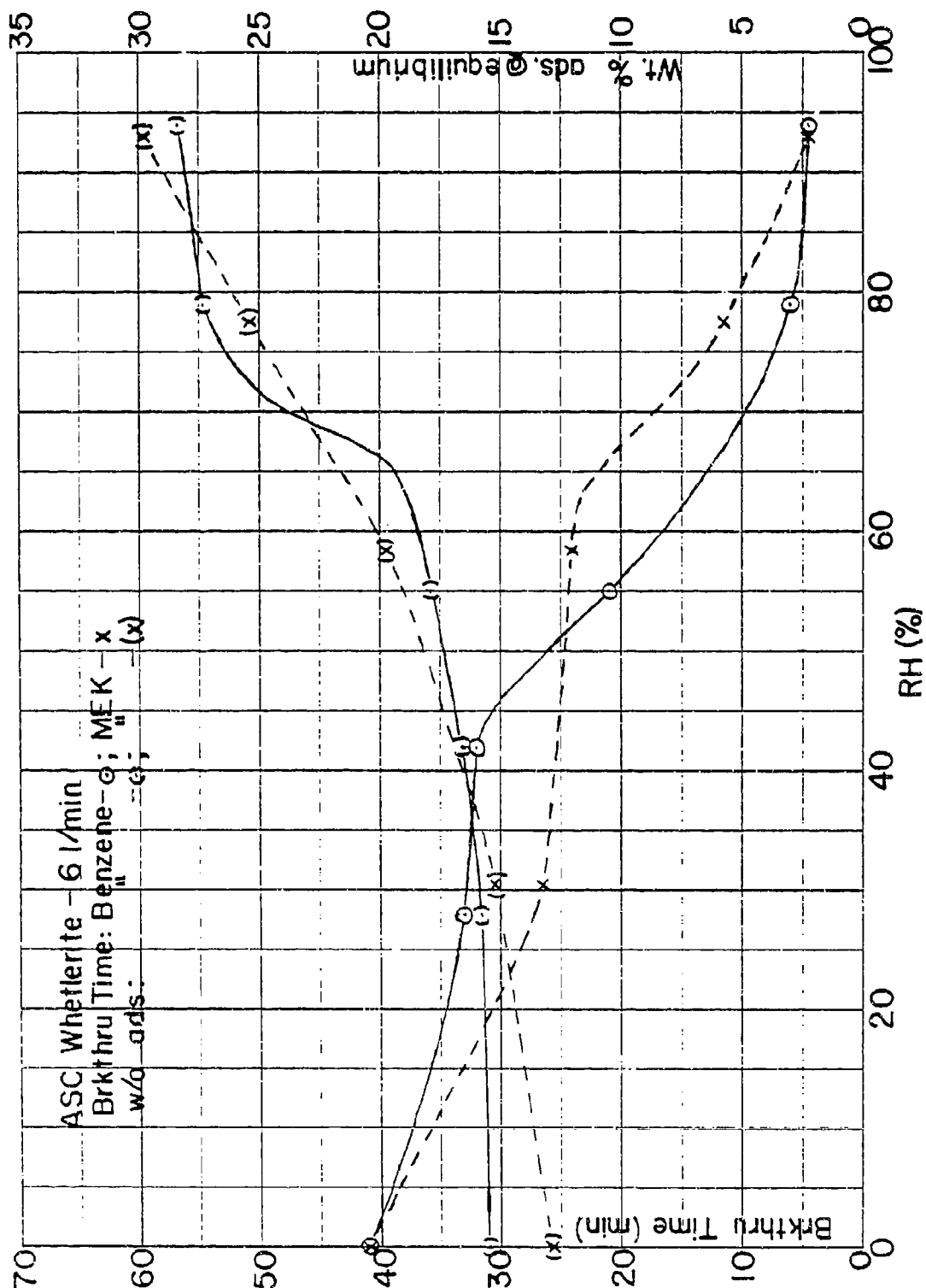


Fig. 5 — Breakthrough time and weight percent adsorbed as functions of relative humidity (ASC Whetlerite, 6 l/min)

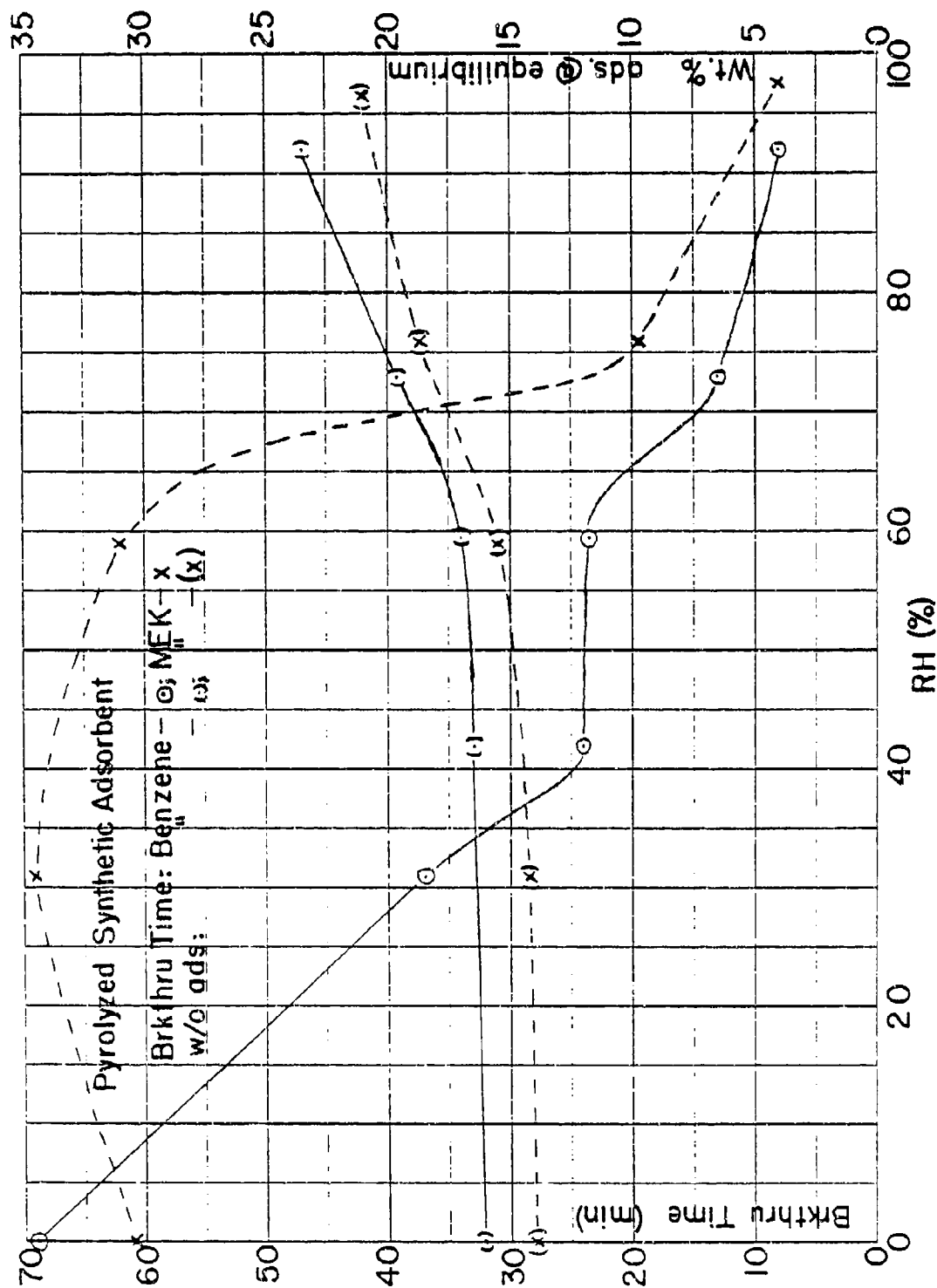


Fig. 6 — Breakthrough time and weight percent adsorbed as functions of relative humidity (Pyrolyzed synthetic adsorbent, 6 l/min)

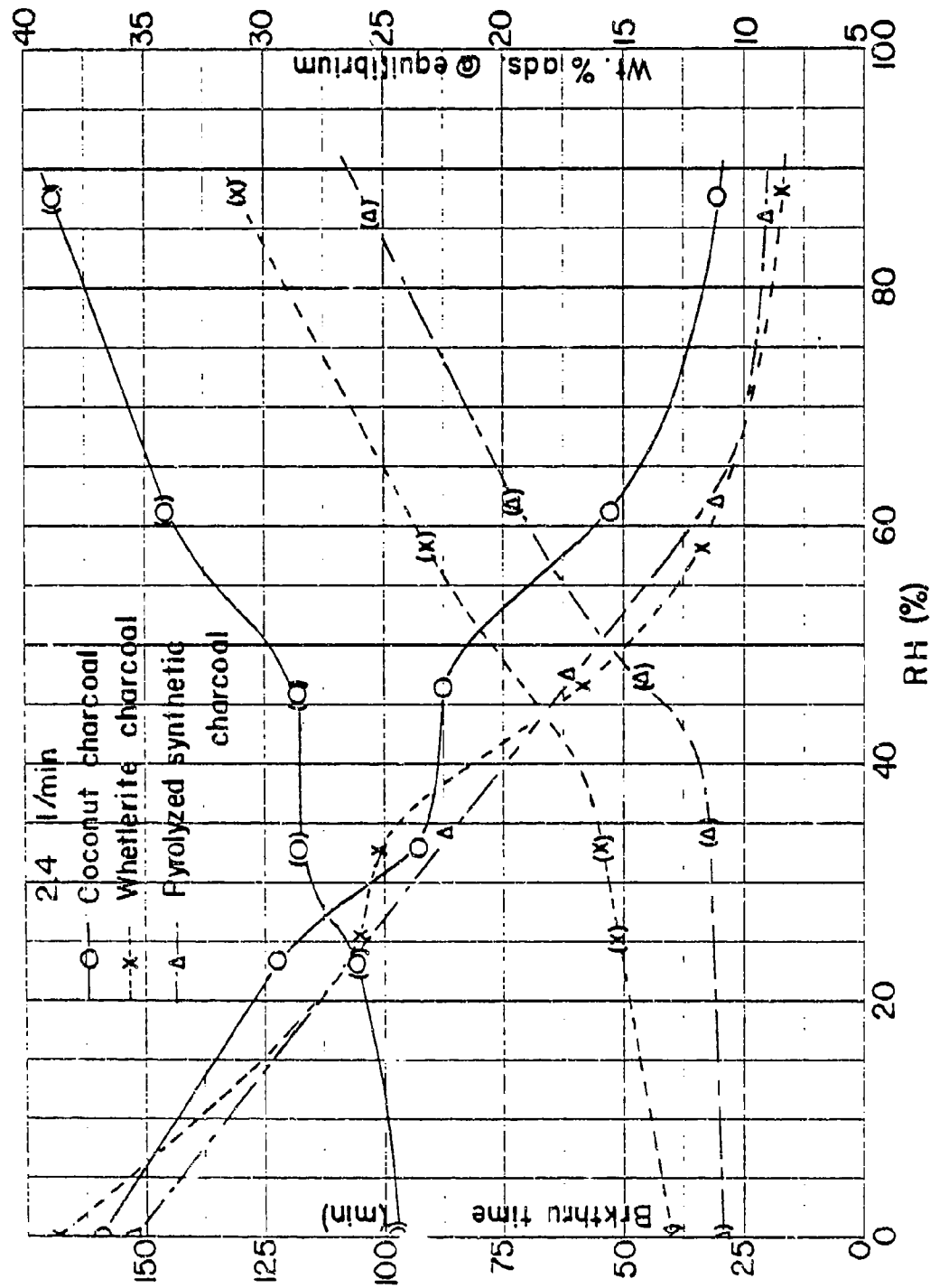


Fig. 7 — Breakthrough time (O, X, Δ) and weight percent adsorbed (O, X, Δ), as functions of relative humidity (3 adsorbents, 2.4 l/min)

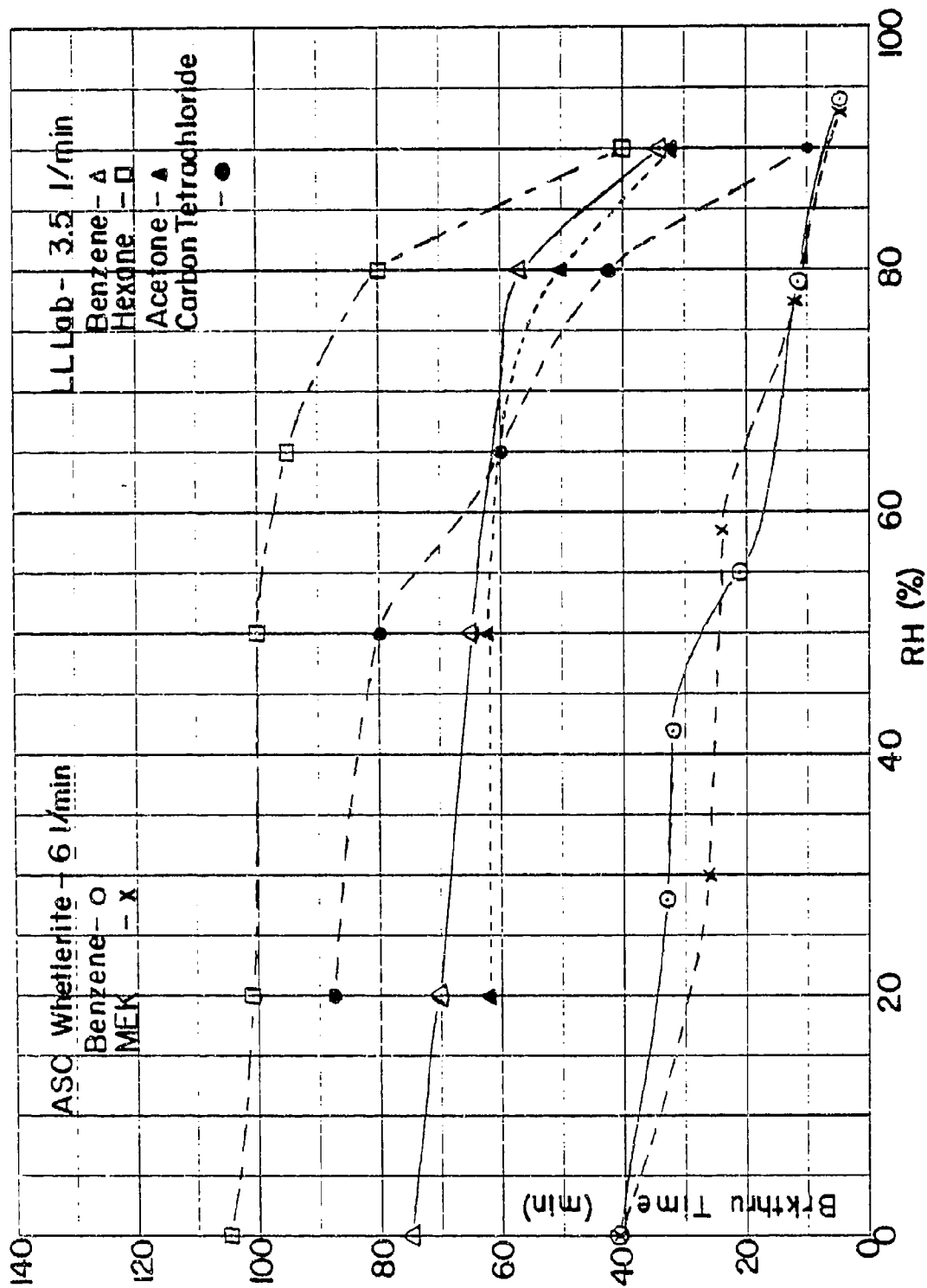


Fig. 8 — Breakthrough time as function of relative humidity (ASC Whetlerite, NRL, 6 l/min; charcoal canisters, LLL, 3.5 l/min)

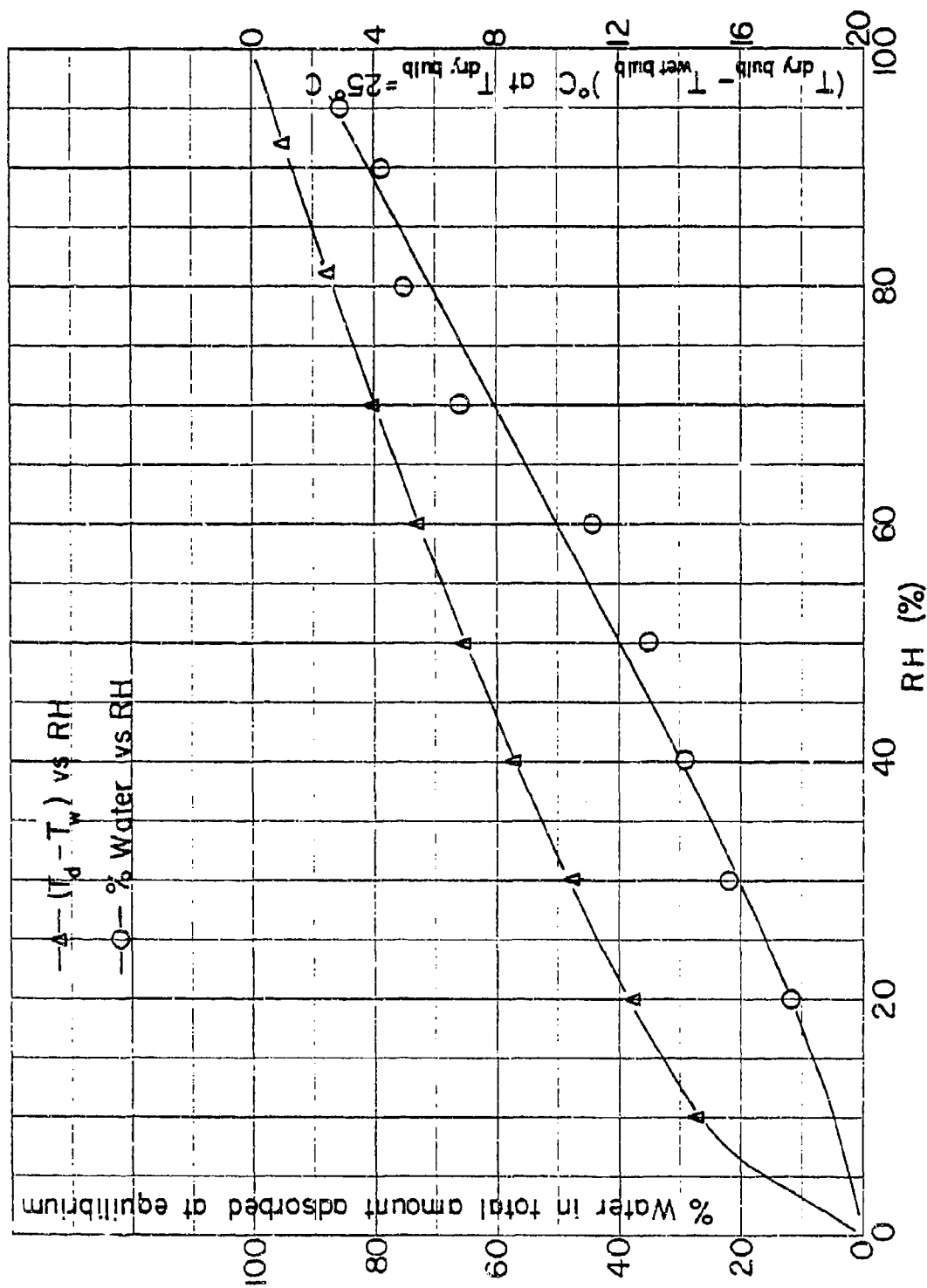


Fig. 9 — Percent water in total adsorbate compared with wet bulb/dry bulb temperature difference as functions of relative humidity